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(54) **Polyethylenic foaming compositions and molded foams**

Polyethylenschäummassen und Formschaumstoffe

Compositions pour mousses de polyéthylénique et mousses formées

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(73) Proprietor:  
**SUMITOMO CHEMICAL COMPANY LIMITED**  
**Osaka-shi, Osaka 541-0041 (JP)**

(72) Inventors:  
• **Sugimoto, Hiroyuki**  
**Osaka 562 (JP)**  
• **Igarashi, Toshio**  
**Kyoto-shi, Kyoto 606 (JP)**  
• **Nakatsuji, Yoshihiro**  
**Toyonaka-shi, Osaka 561 (JP)**  
• **Tatsumi, Masayuki**  
**Tokyo 202 (JP)**

• **Chikanari, Kenzo**  
**Ichihara-shi, Chiba 299-01 (JP)**  
• **Funakoshi, Satoru**  
**Osaka-shi, Osaka 533 (JP)**

(74) Representative:  
**VOSSIUS & PARTNER**  
**Siebertstrasse 4**  
**81675 München (DE)**

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## Description

[0001] The present invention relates to a polyethylenic foaming composition and a method of preparing the same, a polyethylene foam obtained from said polyethylenic foaming composition and a method of preparing the same, a molded composite foam comprising a foam layer obtained from a powder of said polyethylenic foaming composition and a non-foam layer obtained from a powder of a powder composition containing a certain thermoplastic elastomer and a method of preparing the same, a multilayer molded article consisting of a composite foam layer of said molded composite foam and a thermoplastic resin layer and a method of preparing the same, and a multilayer molded article consisting of a composite foam layer as said molded composite foam and a thermosetting resin layer and a method of preparing the same.

[0002] Synthetic resin foams are useful as materials for e.g. shock absorbers, heat insulators and packages, and it is also known that such foams are produced by subjecting a vinyl chloride-based foaming composition powder to a powder molding process.

[0003] However, a foam obtained from a vinyl chloride-based foaming composition powder has not only a relatively high weight but is also not clean in the sense that it emits acidic substances when burned as a waste causing air pollution and acid rain.

[0004] It was already proposed that such problems are overcome by replacing the vinyl chloride-based foaming composition powder with a polyolefinic foaming composition powder consisting of a thermoplastic elastomer as a partially crosslinked composition obtained from an ethylene/ $\alpha$ -olefinic copolymeric rubber and a polyolefinic resin and a foaming agent of a thermal decomposition type for the purpose of obtaining a polyolefinic foam (JP-A-345637-1992).

[0005] Nevertheless, such foam is not always satisfactory due to a poor impact resilience, although it has a high expansion ratio and uniformly foamed cells.

[0006] On the other hand, an attempt was made to prepare a polyethylenic foam by e.g. press molding, extrusion molding or calender molding using a foaming composition consisting of an ethylenic copolymer having functional groups such as carboxylic groups and carboxylic anhydride groups, an ethylenic copolymer having glycidyl groups and a foaming agent of a thermal decomposition type (JP-A-199630-1987).

[0007] However, a foam obtained by such method involves the problems of a poor expansion ratio and a poor impact resilience.

JP-A-49002867

describes crosslinked resin foams, prepared by heat-foaming compositions comprising an ethylene copolymer containing epoxy groups or a mixture of an ethylene copolymer and a polyolefinic resin, a metal powder and/or an inorganic powder as a filler and a blowing agent. The resulting molded articles are melt-deformed if a crosslinking agent such as an organic peroxide is used to prepare a crosslinked polyolefin resin foam.

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refers to a multi-phase thermoplastic composition comprising a blend of (A) a crystalline polyolefin resin forming one phase of the composition and (B) a crosslinked ethylene-containing copolymer forming a second phase of the composition. As crosslinking agent an aromatic or aliphatic dicarboxylic acid is mentioned.

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describes an integrally formed composite foam molded article comprising (I) a non-foam layer and (II) a foamed layer. The non-foam layer is formed from a thermoplastic elastomer powder composition which might be partially crosslinked. As a crosslinking agent, organic peroxide is mentioned.

[0008] It is an object of the invention to provide a synthetic resin foam having a low weight, excellent cleanness, a high expansion ratio and excellent impact resilience.

[0009] This object could be achieved on the basis of the finding that by molding a particular foaming composition consisting of an ethylenic copolymer having glycidyl groups, a carboxylic acid having two or more carboxyl groups and a molecular weight of 1500 or less and a foaming agent of a thermal decomposition type a foam having a high expansion ratio and excellent impact resilience can be obtained.

[0010] On the other hand, a molded composite foam comprising a non-foam layer having a complex surface pattern such as a leather grain pattern and a stitch pattern and a foam layer has conventionally been employed e.g. as a skin for the interior of automobiles. It is known that such skin is made by subjecting a vinyl chloride-type non-foaming composition powder to a powder molding process to form a non-foam layer followed by molding a vinyl chloride-based foaming composition powder into a foam layer as a liner of the non-foam layer.

[0011] However, such molded composite foam obtained from a vinyl chloride-based resin has not only a relatively high weight but also a poor cleanness, and is thus not satisfactory.

[0012] As a molded composite foam capable of overcoming such problems, a molded composite foam having a non-foam layer molded from a composition powder containing a thermoplastic elastomer which is a composition comprising an ethylene/ $\alpha$ -olefinic copolymeric rubber and a polyolefinic resin or a thermoplastic elastomer which is a partially crosslinked composition comprising an ethylene/ $\alpha$ -olefinic copolymeric rubber and a polyolefinic resin and a foam layer molded from a foaming composition powder containing the thermoplastic elastomer mentioned above, and a foaming agent of a thermal decomposition type has already been proposed (JP-A-473-1993, 228947-1993 and 208467-1993).

[0013] Nevertheless, such molded composite foam has an impact resilience which is not sufficient and is not satisfactory although it has a low weight and excellent cleanness as well as a high expansion ratio of the foam layer.

[0014] It is therefore another object of the invention to provide a molded composite foam having excellent impact resilience. This object could be achieved on the basis of the finding that by using a particular foaming composition powder mentioned above consisting of an ethylenic copolymer having glycidyl groups, a carboxylic acid having two or more carboxyl groups and a molecular weight of 1500 or less and a foaming agent of a thermal decomposition type as a foaming composition powder in the powder molding method a molded composite foam having excellent impact resilience as well as a high expansion ratio can be obtained.

[0015] Accordingly, the present invention provides a polyethylenic foaming composition comprising (a) 100 parts by weight of an ethylenic copolymer having glycidyl groups consisting of 20 to 99.9% by weight of an ethylene unit, 0.1 to 30% by weight of the unit of a glycidyl ester of an unsaturated carboxylic acid or an unsaturated glycidyl ether and 0 to 50% by weight of an ethylenically unsaturated ester unit other than glycidyl ester, (b) 0.1 to 30 parts by weight of a carboxylic acid having 2 or more carboxyl groups and a molecular weight of 1500 or less, and (c) 0.1 to 20 parts by weight of a foaming agent of a thermal decomposition type, a method of preparing the same, as well as a polyethylenic foam molded from said polyethylenic foaming composition and a method of preparing the same.

[0016] The present invention also provides a composite foam having excellent impact resilience consisting of a foam layer obtained from the powder of said polyethylenic foaming composition (A) and a non-foam layer obtained from the powder of a composition containing a thermoplastic elastomer (B) shown below, as well as a multilayer molded article having such molded composite foam and a method of preparing the same.

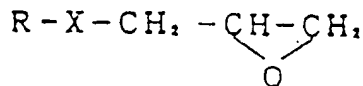
[0017] The thermoplastic elastomer (B) having a complex dynamic viscosity  $\eta^*(1)$  of  $1.4 \times 10^{-4}$  Pa.s ( $1.5 \times 10^5$  poise) or less and a Newtonian viscosity index  $n$  of 0.67 or less is a composition consisting of an ethylene/ $\alpha$ -olefinic copolymeric rubber and a polyolefinic resin or a partially-crosslinked composition consisting of an ethylene/ $\alpha$ -olefinic copolymeric rubber and a polyolefinic resin.

[0018] Moreover, the present invention provides multilayer molded articles as described in claims 7 and 9 and methods of preparing a composite foam and a multilayer molded article as described in claims 6, 8 and 10.

[0019] The present invention is described in detail below.

[0020] The ethylenic copolymer (a) which is a component of the inventive polyethylenic foaming composition employs an ethylenic copolymer having glycidyl groups consisting of 20 to 99.9% by weight of an ethylene unit, 0.1 to 30% by weight of the unit of a glycidyl ester of an unsaturated carboxylic acid or an unsaturated glycidyl ether and 0 to 50% by weight of an ethylenically unsaturated ester unit other than glycidyl ester.

[0021] As a unit of a glycidyl ester of an unsaturated carboxylic acid or an unsaturated glycidyl ether, a unit derived from a compound of a general formula:



wherein R represents an alkenyl group having 2 to 18 carbon atoms, X represents a carbonyloxy group, methyleneoxy group or phenyleneoxy group, may be contemplated.

[0022] Examples of such compounds include glycidyl acrylate, glycidyl methacrylate, glycidyl itaconate, allyl glycidyl ether, methallyl glycidyl ether and styrene-p-glycidyl ether.

[0023] The ethylenic copolymer contains the unit of a glycidyl ester of an unsaturated carboxylic acid or the unit of an unsaturated glycidyl ether generally in an amount from 0.1 to 30% by weight, preferably from 0.5 to 20% by weight.

[0024] As an ethylenically unsaturated ester unit other than glycidyl ester, a unit derived from vinyl esters such as vinyl acetate and vinyl propionate and from esters of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate and butyl methacrylate can be mentioned. The units derived from vinyl acetate, methyl acrylate and ethyl acrylate are preferred.

[0025] Although an ethylenically unsaturated ester unit other than glycidyl ester is not necessarily be contained in

an ethylenic copolymer, it may be contained in an amount of 50% by weight or less. An amount exceeding 50% by weight causes not only reduced thermal resistance of a molded article but also significantly affected powder fluidability resulting in difficulty in powder molding process. Thus, a content of 50% by weight is practical when such ethylenically unsaturated ester unit is contained.

**[0026]** The ethylenic copolymer (a) contains the monomer units mentioned above, and it can be produced, for example, by copolymerizing the starting monomers in the presence of a radical initiator under a pressure from 500 to 4000 atm and at a temperature from 100 to 300°C in the presence or absence of a solvent or chain transfer agent. Alternatively, it may be produced by subjecting a mixture consisting e.g. of polyethylene, an unsaturated compound having glycidyl groups and a radical initiator to melt graft polymerization using, for example, an extruder.

**[0027]** The ethylenic copolymer (a) having a melt flow rate (MFR, according to JIS K6730) of 5 g/10 minutes or higher is generally employed since a rate less than 5 g/10 minutes tends to reduce the expansion ratio. It is preferable to use an ethylenic copolymer (a) having a MFR of 10 g/10 minutes or more.

**[0028]** The carboxylic acid (b) employed in this invention has two or more carboxylic groups and a molecular weight of 1500 or less, preferably 1000 or less. It may be in a form of a solid or a liquid.

**[0029]** Examples are oxalic acid maleic acid, malonic acid, phthalic acid, fumaric acid, succinic acid and derivatives therefrom such as 2,3-dimethyl succinic acid, 2-ethyl-2-methyl succinic acid, 2-phenyl succinic acid and 2-hydroxy succinic acid, glutaric acid and derivatives therefrom such as 3-methyl glutaric acid, 2,4-dimethyl glutaric acid and 3,3-dimethyl glutaric acid, adipic acid and derivatives therefrom such as 3-methyl adipic acid, sebacic acid, 1,4-cyclohexane dicarboxylic acid, phthalic acid derivatives such as terephthalic acid and 5-hydroxyisophthalic acid, benzene-tricarboxylic acids such as 1,3,5-benzenetricarboxylic acid and 1,2,4-benzenetricarboxylic acid, propanetricarboxylic acids such as 2-phenyl-1,2,3-propanetricarboxylic acid, 1-phenyl-1,2,3-propanetricarboxylic acid, 2-hydroxy-1,2,3-propanetricarboxylic acid and 3-hydroxy-1,2,3-propanetricarboxylic acid and pyromellitic acid. Among these, those having a primary acid dissociation constant in water of  $50 \times 10^{-5}$  or less are preferably employed.

**[0030]** The carboxylic acid (b) is employed in an amount from 0.1 to 30 parts by weight, preferably from 1 to 20 parts by weight based on 100 parts by weight of the ethylenic copolymer (a). An amount less than 0.1 parts by weight causes insufficient crosslinking, and a foam having satisfactory impact resilience can not be obtained. An amount exceeding 30 parts by weight causes excessive crosslinking, resulting in a reduced expansion ratio whereby producing a hard foam having poor impact resilience.

**[0031]** As the foaming agent of a thermal decomposition type (c), a foaming agent having a decomposition temperature higher than the melting temperature of the ethylenic copolymer (a) is employed. For example, a foaming agent having a decomposition temperature from about 120 to 230°C, preferably from about 150 to 230°C is employed.

**[0032]** Examples are azo compounds such as azodicarbonic amide, 2,2'-azobisisobutyronitrile and diazodiaminobenzene, sulfonyl hydrazide compounds such as benzene sulfonyl hydrazide, benzene-1,3-sulfonyl hydrazide, diphenylsulfone-3,3'-disulfonyl hydrazide, diphenyloxide-4,4'-disulfonyl hydrazide, 4,4'-oxybis(benzenesulfonyl hydrazide) and p-toluene sulfonyl hydrazide, nitroso compounds such as N,N'-dinitrosopentamethylenecetramine and N,N'-dinitroso-N,N'-dimethyl terephthalic amide, azide compounds such as terephthalic azide and p-t-butyl benzazide as well as carbonates such as sodium bicarbonate, ammonium bicarbonate and ammonium carbonate. Among these, azodicarbonic amide is preferably employed.

**[0033]** The foaming agent of a thermal decomposition type (c) is employed generally in an amount from 0.1 to 20 parts by weight, preferably from 5 to 10 parts by weight based on 100 parts by weight of the ethylenic copolymer (a).

**[0034]** A polyethylenic foaming composition according to the present invention characterized in that it contains the ethylenic copolymer (a), the carboxylic acid (b) and the foaming agent of a thermal decomposition type as mentioned above, may further contain, if necessary, other components, including heat resistance stabilizers such as phenol-, sulfide-, phosphite, amine- or amide-based stabilizers, anti-aging agents, anti-weathering stabilizers, antistatic agents, metallic soaps, lubricant, pigments as well as foaming aids, anti-foaming agents, liquid coatings and a mold release agent.

**[0035]** Such components may be incorporated using e.g. an open roll blender, high-shear rotating mixer, Banbury mixer or a kneader, at a temperature which is lower than the decomposition temperature of the foaming agent of a thermal decomposition type (c) but does not cause crosslinking between the ethylenic copolymer (a) and the carboxylic acid (b) in a standard method such as a mixing procedure while keeping the ethylenic copolymer (a) in a state of the ethylenic copolymer (a) being powder or a melt mixing procedure. The polyethylenic foaming composition of the present invention may be produced in various forms such as a mass, powder, pellet and a sheet depending on a particular use.

**[0036]** For example, in case of producing a polyethylenic foaming composition powder (A) for use in a powder molding, a blender fitted with a jacket or a high-shear rotating mixer is usually employed. A preferred mixer is one capable of preventing blocking of the powder particles by means of applying the shear stress, such as a high-shear rotating mixer. In such case, for the purpose of prevention of heat fusion of the powder particles due to shear heat generation, the mixing is generally conducted while cooling by circulating a coolant through the jacket. In such case, a powder which was previously been pulverized is employed as the ethylenic copolymer (a). The mean particle size is generally 32 mesh

size (passing through a square pore of 500  $\mu\text{m}$  x 500  $\mu\text{m}$ ), preferably 40 mesh size (passing through a square pore of 355  $\mu\text{m}$  x 355  $\mu\text{m}$ ) to 100 mesh size (passing through a square pore of 150  $\mu\text{m}$  x 150  $\mu\text{m}$ ), when determined using Tyler standard sieves. When a carboxylic acid (b) in form of a solid is employed a powder having a particle size of 100  $\mu\text{m}$  or less is generally employed. When a carboxylic acid as a liquid is employed, it is admixed first with the ethylenic copolymer (a) and then with the foaming agent of a thermal decomposition type (c).

[0037] Alternatively, the powder (A) may also be obtained by melt mixing the ethylenic copolymer (a), the carboxylic acid (b), the foaming agent of a thermal decomposition type (c) and other components at a temperature which is lower than the decomposition temperature of the foaming agent (c) but does not cause the crosslinking between the copolymer (a) and the carboxylic acid (b) using an extruder followed by pulverizing the cooled composition at the glass transition temperature or below. In such case, the mean particle size of the powder (A) is adjusted generally to 32 mesh size or less, preferably 40 to 100 mesh size when determined using Tyler standard sieves.

[0038] To mold the powder (A), powder molding methods such as, for example, a fluidized immersion method, powder sintering method, electrostatic coating method, powder flame-spray method, powder rotational molding method, and a powder slush molding method (JP-A 132507-1983) are employed and the powder slush molding method is especially preferred.

[0039] When the powder slush molding method is employed, a molded foam can be produced via process (1) wherein a vessel containing a required amount of the powder (A) and having an opening and a mold which has been heated to a temperature sufficiently higher than the melting temperature of the ethylenic copolymer (a) and which has an opening are attached to each other at their openings or the former is inserted and immobilized in the cavity of the latter, and the unit thus assembled is rotated or shaken to supply the powder rapidly into the entire region of the cavity whereby achieving adhesion of the powder to the internal wall of the mold followed by melting, and then excessive powder (A) is drained out into the vessel, followed by process (2) wherein the molded article obtained in process (1) is foamed by heating.

[0040] The mode of heating of the mold employed in the powder molding method is not particularly specified, and the gas-fired furnace system, the hot medium oil circulation system, the hot medium oil or hot fluidized sand immersion system, or the high-frequency induction heating system be employed, and these methods may be utilized also in the process of the foaming of the melted foaming composition.

[0041] The temperature of the mold at which the powder (A) is deposited and melted on the internal wall of the mold is higher usually by 50 to 200°C, preferably by 80 to 170°C than the melting temperature of the ethylenic copolymer (a), for example, 140 to 310 °C, preferably 170 to 280°C. The time period of the deposition and the melting is not particularly specified, and may vary depending on the size and the thickness of the molded article.

[0042] The temperature at which the foaming is effected should be within the range of 100°C, preferably within the range of 80°C, above the decomposition temperature of the foaming agent of a thermal decomposition type (c). The time period of the foaming is not specifically limited, and may vary depending on the thickness and the expansion ratio of the molded foam.

[0043] When a composition in a form of a bulk or a pellet obtained by melt mixing is employed, the composition may be molded by e.g. an extrusion molding method, calender molding method, pressing method and an injection molding method into e.g. a panel, pipe, film and a sheet, and then subjected to the foaming by heating in atmospheric pressure or under pressure.

[0044] For example, in case of producing a foam sheet by the pressing method, the pressurized one shot method and the pressurized two shot method are usually employed.

[0045] In the pressurized one shot method, a sheet is formed by a press molding machine. This molding is effected at a temperature lower than the decomposition temperature of the foaming agent of a thermal decomposition type (c) and higher usually by 10 to 50°C, preferably by 10 to 30°C, than the melting temperature of the ethylenic copolymer (a). The pressure to be applied is usually 0 to 100  $\text{kg/cm}^2 \cdot \text{G}$ , and the time period is usually about 0.5 to 10 minutes.

[0046] After formation of the sheet, the press molding machine is further operated to heat the sheet at a temperature not lower than the decomposition temperature of the foaming agent for a predetermined period under pressure, and subsequently the pressure is withdrawn whereby effecting the foaming. The temperature of heating may vary depending on the type of the foaming agent employed, and is higher usually by 0 to 100°C, preferably by 20 to 50°C than the decomposition temperature of the foaming agent. The pressure to be applied is usually 0 to 100  $\text{kg/cm}^2 \cdot \text{G}$ , and the time period is usually about 0.5 to 10 minutes.

[0047] In the pressurized two shot method, after formation of the sheet, the press molding machine is further operated to heat the sheet under pressure for a predetermined period to allow the crosslinking reaction between the ethylenic copolymer (a) and the carboxylic acid (b) to proceed. The sheet is cooled once and then heated again under pressure. Withdrawal of the pressure results in a molded foam.

[0048] The first shot is conducted usually under a condition which allows the crosslinking between the ethylenic copolymer (a) and the carboxylic acid (b) to proceed but does not cause the decomposition of the foaming agent of a thermal decomposition type (c), while the second shot is conducted usually under a condition which allow the decom-

position of the foaming agent of a thermal decomposition type (c).

[0049] The temperature of heating is usually within the range of  $\pm 30^\circ\text{C}$  with regard to the decomposition temperature of the foaming agent (c) of a thermal decomposition type. The pressure to be applied is usually 0 to  $100 \text{ kg/cm}^2 \cdot \text{G}$ , and the time period is usually about 0.1 to 10 minutes.

5 [0050] When the molded article is detached from the mold, problems such as folding wrinkle may occur. To avoid such problems, it is effective to spray a fluorine- or silicon-based mold release agent onto the mold prior to the molding. When a relatively simple-shaped mold, such as a plate, is employed, a lining of a fluorine-based resin sheet may be advantageous.

10 [0051] It is also advantageous to incorporate a polymethylsiloxane compound as an internally added mold release agent into the composition, especially in case of a continuous production. Such compound usually has a viscosity at  $25^\circ\text{C}$  of  $2.0 \times 10^{-5} \text{ m}^2/\text{s}$  (20 centistokes) or higher, preferably from  $5.0 \times 10^{-5}$  to  $5.0 \times 10^{-3} \text{ m}^2/\text{s}$  (50 to 5000 centistokes), and is employed usually in an amount of 2 parts by weight based on 100 parts by weight of the ethylenic copolymer (a). An amount greater than 2 parts by weight may affect the heat fusion of the composition, resulting in a molded article having a poor mechanical property and causing a staining of the mold due to the bleeding of the mold release agent

15 out onto the surface of the mold.  
[0052] On the other hand, by the procedure similar as in the process (1) of the powder slush molding method described above except for employing a powder composition containing the thermoplastic elastomer (B) shown below instead of the polyethylenic foaming composition powder (A), a non-foam layer is formed on the mold, and then by using this mold having the non-foam layer on it, the powder (A) is molded as a foam on the non-foam layer by the process (1) and the process (2), a composite foam in which the non-foam layer and the foam layer are integrated can be produced. To produce such composite foam, the methods other than the powder slush molding, for example, a fluidized immersion molding method, powder sintering method, electrostatic coating method, powder flame-spray method and a powder rotational molding method may also be employed but the powder slush molding method is preferred.

20 [0053] The thermoplastic elastomer (B) having a complex dynamic viscosity  $\eta^*$  of  $1.4 \times 10^4 \text{ Pa}\cdot\text{s}$  ( $1.5 \times 10^5$  poise) or less and a Newtonian viscosity index  $n$  of 0.67 or less is a composition consisting of an ethylene/ $\alpha$ -olefinic copolymeric rubber and a polyolefinic resin or a partially-crosslinked composition consisting of an ethylene/ $\alpha$ -olefinic copolymeric rubber and a polyolefinic resin.

25 [0054] As an ethylene/ $\alpha$ -olefinic copolymeric rubber which is a component of the thermoplastic elastomer (B), rubbers containing an olefin as a major component, such as an ethylene/ $\alpha$ -olefinic copolymeric rubber and an ethylene/ $\alpha$ -olefin/non-conjugate diene copolymeric rubber may be contemplated. Examples of the  $\alpha$ -olefin are propylene and 1-butene, and examples of the non-conjugate diene are dicyclopentadiene, ethylidene norbornene, 1,4-hexadiene, cyclooctadiene and methylene norbornene.

30 [0055] Among these ethylene/ $\alpha$ -olefinic copolymeric rubbers, ethylene/propylene/ethylidene norbornene copolymeric rubber (hereinafter referred as EPDM) is more preferably employed, and, when incorporated into an elastomer, provides a composite foam having excellent heat resistance and showing sufficient impact resilience of the foam layer.

35 [0056] Mooney viscosity (Mooney viscosity determined at  $100^\circ\text{C}$  ( $\text{ML}_{1+4}$   $100^\circ\text{C}$ ) according to ASTM D-927-57T) of the ethylene/ $\alpha$ -olefinic copolymeric rubber is usually within the range from 130 to 350, preferably from 200 to 300.

40 [0057] The ethylene/ $\alpha$ -olefinic copolymeric rubber may be employed also in form of an oil extended rubber obtained by admixing a mineral oil-based softener such as paraffin-based process oil. In such case, the melt fluidity is increased and the pliability of the molded article is also increased. The amount of the mineral oil-based softener is usually up to 120 parts by weight, preferably 30 to 120 parts by weight based on 100 parts by weight of the ethylene/ $\alpha$ -olefinic copolymeric rubber.

45 [0058] As the polyolefinic resin which is the other component of the thermoplastic elastomer (B) polypropylene, propylene/ethylene copolymer and a copolymer of propylene with  $\alpha$ -olefins other than propylene are preferably employed. Especially when a copolymeric resin of propylene with 1-butene is employed, the hardness of the molded article can also be reduced.

50 [0059] Since the heat fusion of the powder during the powder molding process becomes insufficient and the strength of the molded article thus obtained becomes lower when the melt flow rate (MFR, determined at  $230^\circ\text{C}$  with 2.16 kg loading according to JIS K-7210) of the polyolefinic resin is less than 20 g/10 minutes, a resin having MFR of 20 g/10 minutes or more is generally employed. Preferably, MFR is 50 g/10 minutes.

[0060] The thermoplastic elastomer (B) employed in the present invention is a composition of the ethylene/ $\alpha$ -olefinic copolymeric rubber and the polyolefinic resin or a partially crosslinked composition obtained by crosslinking the composition as described above. The weight ratio of the ethylene/ $\alpha$ -olefinic copolymeric rubber and the olefinic resin is preferably 5:95 to 80:20.

55 [0061] To produce a partially crosslinked composition, an organic peroxide is usually employed as a crosslinking agent. When an organic peroxide is employed, dialkylperoxide is preferably employed. Dynamic crosslinking in the presence of a crosslinking aid such as a bismaleimide compound using a trace amount of an organic peroxide is preferable, and in such case, the suitable crosslinking degree of the ethylene/ $\alpha$ -olefinic copolymeric rubber provides

improved heat resistance as well as increased fluidity. The crosslinking agent is employed in an amount of 1.5 parts by weight or less, preferably 0.6 parts by weight or less based on 100 parts by weight of the total amount of the ethylene/ $\alpha$ -olefinic copolymeric rubber and the polyolefinic resin, and the organic peroxide is employed in an amount of 0.2 parts by weight or less, preferably 0.1 parts by weight or less, and more preferably 0.07 parts by weight or less.

5 [0062] As a method of the dynamic crosslinking, a continuous kneading extruder method, such as single- or twin-screw kneading extruder may preferably be employed. When the twin-screw kneading extruder is employed, the extrusion crosslinking when conducted at a shear rate less than  $1 \times 10^3 \text{ sec}^{-1}$  provides a larger particle size of the distributed particles of the ethylene/ $\alpha$ -olefinic copolymeric rubber, resulting in difficulty in realizing the viscosity condition of the present invention. Accordingly, it is preferable to conduct the continuous extrusion crosslinking at a shear rate of  $1 \times 10^3 \text{ sec}^{-1}$  or higher.

10 [0063] The thermoplastic elastomer (B) in the present invention has a complex dynamic viscosity  $\eta^*$  (1) of  $1.5 \times 10^4 \text{ Pa.s}$  ( $1.5 \times 10^5 \text{ poise}$ ) or less, preferably  $1.0 \times 10^4 \text{ Pa.s}$  ( $1.0 \times 10^5 \text{ poise}$ ) or less, and a Newtonian viscosity index  $n$  of 0.67 or less, preferably 0.60 or less.

[0064] The complex dynamic viscosity  $\eta^*$  (1) is a value determined at  $250^\circ\text{C}$  at a frequency of 1 radian/sec. When this value exceeds  $1.5 \times 10^4 \text{ Pa.s}$  ( $1.5 \times 10^5 \text{ poise}$ ), the composition powder containing the elastomer (B) is not melt-fluidized on the surface of the mold, and can not be molded by the powder molding method in which the shear rate during the process is as low as  $1 \text{ sec}^{-1}$  or less.

[0065] The Newtonian viscosity index  $n$  is a value calculated from the complex dynamic viscosity  $\eta^*$  (1) mentioned above and the complex dynamic viscosity  $\eta^*$  (100) determined at the frequency of 100 radian/sec using the following formula:

$$n = \log\{\eta^* (1) / \eta^* (100)\} / 2$$

[0066] When the Newtonian viscosity index  $n$  exceeds 0.67, the dependency of the complex dynamic viscosity on the frequency is too high even if the complex dynamic viscosity  $\eta^*$  (1) is  $1.5 \times 10^4 \text{ Pa.s}$  ( $1.5 \times 10^5 \text{ poise}$ ) or less, and the powder molding method in which the compaction pressure upon molding is as low as  $1 \text{ kg/cm}^2$  or less only provides a molded article having a low mechanical property due to the insufficient heat fusion of the composition powder.

[0067] When a partially-crosslinked composition is employed as a thermoplastic elastomer (B) in the present invention, a non-crosslinked ethylene/ $\alpha$ -olefinic copolymeric rubber or ethylene/ $\alpha$ -olefinic copolymeric resin may be blended in an amount of 50 parts by weight or less to the 100 parts by weight of the elastomer for the purpose of improvement in pliability of the molded article. In such case, propylene and 1-butene are employed independently or in a mixture as the  $\alpha$ -olefin. An ethylene/propylene copolymeric rubber having an ethylene content from 40 to 90% by weight, preferably from 70 to 85% by weight and having  $ML_{1+4}$   $100^\circ\text{C}$  of 50 or less is preferred.

[0068] The composition powder containing the thermoplastic elastomer (B) in the present invention is usually prepared by pulverizing the composition containing the thermoplastic elastomer (B) at a low temperature, the glass transition temperature or below. For example, a freeze pulverization method using liquid nitrogen is preferably employed. A pellet of the composition containing the thermoplastic elastomer (B) which is cooled to  $-70^\circ\text{C}$  or below, preferably  $-90^\circ\text{C}$  or below may be pulverized mechanically using an impact type pulverizer such as a ball mill. When the pellet is pulverized at a temperature higher than  $-70^\circ\text{C}$ , the particle size becomes greater resulting in poor powder moldability. In order to prevent the temperature of the composition from being raised to the glass transition temperature or higher during the pulverizing operation, it is preferable that the internal temperature of the pulverizer such as a ball mill is kept at approximately  $-120^\circ\text{C}$  during pulverization. It is also preferred that the pulverizer itself is cooled externally. Pulverization is preferably conducted so that 95% or more of the total weight of the composition powder containing the thermoplastic elastomer (B) obtained passes through the 32 mesh screen of a Tyler standard sieve. When powder having a size greater than 32 mesh size is present in an amount exceeding 5% by weight, a uniform thickness may not be obtained in the powder molding. Absence of the uniformity in the thickness leads to the absence of uniformity in the pliability of the molded article, which may cause the folding wrinkle, resulting in poor commercial value of the molded article.

[0069] The composition powder containing the thermoplastic elastomer (B) in the present invention may contain an internally added mold release agent, which may be polymethylsiloxane compound.

50 [0070] In such case, the polymethylsiloxane compound preferably has a viscosity at  $25^\circ\text{C}$  of  $2.0 \times 10^{-5} \text{ m}^2/\text{s}$  (20 centistokes) or higher, more preferably from  $5.0 \times 10^{-5}$  to  $5.0 \times 10^{-3} \text{ m}^2/\text{s}$  (50 to 5000 centistokes). An excessively high viscosity may reduce the releasing effect.

[0071] The internally added mold release agent is incorporated in an amount of 2 parts by weight or less per 100 parts by weight of the composition powder. An amount greater than 2 parts by weight affect the heat fusion of the powder, resulting in a molded article having a poor mechanical property as well as a risk of the staining of the mold due to the bleeding of the mold release agent out onto the surface of the mold.

[0072] The internally added mold release agent may be added before or after the pulverization.

[0073] The composition powder containing the thermoplastic elastomer (B) in the present invention may contain

heat resistant stabilizers such as phenol-, sulfide-, phenylalkane-, phosphite-, amine- or amide-based stabilizers, anti-aging agents, anti-weathering stabilizers, antistatic agents, metallic soaps, lubricant such as wax and colouring pigments. These additives may be incorporated before or after the pulverization.

[0074] When a molded composite foam is prepared by the powder slush molding method, (1) a vessel containing the composition powder containing the thermoplastic elastomer (B) and a mold which has been heated to a temperature sufficiently higher than the melting temperature of the elastomer (B) and which has a complex emboss pattern on the internal wall are integrated with each other and the unit thus assembled is rotated or shaken to effect the adhesion of the powder to the internal wall of the mold followed by melting and draining the non-melted excessive powder off, (2) then the vessel is taken out, and a vessel containing the polyethylenic foaming composition powder (A) and a mold which has been heated to a temperature sufficiently higher than the melting temperature of the ethylenic copolymer (a) and on which the non-foam layer obtained in the preceding step has been mounted are integrated similarly, and the unit thus assembled is moved similarly to effect the adhesion of the powder (A) onto the non-foam layer on the mold followed by melting and draining the non-melted excessive powder off into the vessel, and (3) subsequently, the vessel is taken out and the molded article is foamed while heating.

[0075] The molded composite foam of the present invention may have the composite multilayer consisting of non-foam layer/foam layer/non-foam layer. In such case, the processes (1) and (2) described above are conducted, and then the process (1) is conducted again and subsequently the process (3) is conducted to obtain such a multilayer.

[0076] In addition, a intermediate layer obtained from a non-foaming composition which is the polyethylenic foaming composition powder (A) excluding the foaming agent of a thermal decomposition type (c) may be provided between the non-foam layer and the foam layer. In such case, a composite foam having excellent adhesion of the non-foam layer and the foam layer is obtained.

[0077] The mode of heating of the mold in the powder molding for production of the molded composite foam described above is not particularly specified, and various methods mentioned above may be employed.

[0078] The powder molding temperature in the production of the molded composite foam is generally 160 to 300°C, preferably 180 to 280°C. The time period of the molding is not limited specifically, and may vary depending on the size and the thickness of the molded article. The temperature at which the foaming composition is foamed is generally 180 to 280°C, preferably 180 to 260°C. The time period of the foaming is not limited specifically, and may vary depending on the thickness and the expansion ratio of the foam layer.

[0079] Since the molded composite foam of the present invention thus obtained has excellent lightness in weight and cleanness, increased expansion ratio of the foam layer and excellent impact resilience, it can widely be used in various applications. Among them, it may preferably be employed as a top layer of a multilayer molded article.

[0080] As a multilayer molded article having the molded composite foam as a top layer according to the present invention, a multilayer molded article having as a substrate material a thermoplastic resin such as polypropylene, propylene/α-olefinic copolymer, propylene/ethylene copolymer, polystyrene-based resin, polyethylenic resin and methacrylic resin and a thermosetting resin such as semi-rigid urethane, rigid urethane and epoxy resin may be contemplated. A preferred thermoplastic resin is polypropylene while a preferred thermosetting resin is rigid urethane.

[0081] To the thermoplastic resin employed in the present invention, various additives such as fillers, non-filler and glass fibers, pigments, lubricants, antistatic agents and a stabilizer may be incorporated, if desired.

[0082] In a method of integrating the top layer and the thermoplastic resin layer, the top layer obtained, for example, by the powder molding method, is integrated to a mold base in a male or a female mold for the compression molding while being retained on the mold for the powder molding, and the molten thermoplastic resin is supplied to a cavity between the exposed surface of the top layer and the male or female mold. Then the male mold and the female mold are pressed to each other whereby achieving the integration of the top layer and the thermoplastic resin layer. Since the top layer on which the emboss pattern of the molds has been transferred is subjected to the molding of the thermoplastic resin while being retained on the mold, a multilayer molded article can be obtained without affecting the pattern on the top layer.

[0083] The mold for the top layer and the mold for the thermoplastic resin layer are not necessarily the same. For example, the top layer may be released from the mold therefor and then retained in one of the male and female molds. Then the molten thermoplastic resin is fed to the cavity between the top layer and the other mold. Then by pressing the both molds to each other, the top layer is integrated with the thermoplastic resin layer.

[0084] To feed the molten thermoplastic resin, it is preferable to press the molds to each other after or during feeding. In such case, a multilayer molded article can be obtained in which the top layer exhibits less deviation and more excellent transfer of the pattern when compared with that obtained by a method wherein the resin is fed to the mold which has already been pressed to each other.

[0085] The method of feeding of the molten thermoplastic resin is not specifically limited. For example, the resin may be fed via a resin inlet provided in a mold facing the back of the top layer. Alternatively, a nose for supplying the molten resin is inserted into the cavity between the male mold and the female mold to feed the molten resin, and then, after feeding, the nose for supplying is drawn out of the system and then the both molds are closed. Lateral pressing of



the molds may also be employed.

[0086] As a male mold and a female mold, the molds capable of being slid on each other at their circumference whereby effecting the closing may be employed. When the clearance of the sliding surfaces between the both molds is almost equal to the thickness of the top layer, the molding is completed while leaving the top layer material at the edge of the article to allow the folding back of the remaining top layer material, whereby obtaining an article whose external circumference is covered entirely with the top layer material.

[0087] In a method of integrating the top layer and the thermo-setting resin layer consisting of, for example, urethane, the top layer obtained by the powder molding is retained on the mold for the powder molding while the mixture of polyol, setting catalyst such as amine and polyisocyanate is poured into the cavity whereby effecting the setting.

[0088] Since the multilayer molded article thus obtained according to the present invention has excellent lightness in weight, excellent cleanness, excellent impact resilience and sophisticated appearance, it can be used in a wide range of applications.

[0089] In the field of automobile industries, the present molded multilayer article can be useful in Interior top layer materials of e.g. an instrument panel, console box, arm rest, head rest, door trim, rear panel, pillar trim, sunvisor, trunk-room trim, trunklid trim, airbag housing, sheet buckle, headliner, glove compartment, steering wheel cover, and a ceiling, and interior molded articles of e.g. a kicking plate, change lever bouts and a ceiling, and exterior parts such as a spoiler, side mall, number plate housing, mirror housing, airdom skier and a matguard.

[0090] In the field of domestic electric instruments and office automation instruments, the present molded multilayer article is useful in exterior materials of e.g. a television monitor, video tape recorder, automatic laundry washer, laundry drier, cleaner and a air conditioner.

[0091] In the field of sport recreational items, the present molded multilayer article is useful in interior materials of a boat, and in beach recreational items. In the field of architecture and house building, it is useful e.g. in furnitures, desk, chair, gate, door, fence, wall ornament, ceiling ornament and the floor of a kitchen and a restroom.

[0092] It is useful also in industrial materials and notions.

[0093] By using the polyethylenic foaming composition of the present invention, a foam having excellent lightness in weight, excellent cleanness, uniform foam cells, high expansion ratio and excellent impact resilience can be obtained.

[0094] Since the molded composite foam of the present invention has excellent lightness in weight, excellent cleanness, excellent impact resilience and high expansion ratio of the foam layer, it can be applied in various fields. The molded composite foam having the foam layer as the outer layer is preferably employed as a top layer material of a multilayer molded article since it exhibits excellent adhesion to the resin used as the substrate.

[0095] The present invention is further described in the following examples which are not intended to restrict the scope of the present invention in any way.

[0096] In the examples and comparative examples, appearance of a molded foam, state of foam cells, expansion ratio and impact resilience are evaluated as follows.

#### Appearance of the molded foam

[0097] A molded foam was observed macroscopically and evaluated as follows.

- ⊙: Uniform foaming without variation in thickness
- o: Almost uniform foaming with some variation in thickness
- X: Variable foaming with great variations in thickness

#### State of the foam cells

[0098] Sectional surface of a molded foam was observed macroscopically and evaluated as follows.

- ⊙: Uniform cells
- o: Slightly variable cells
- X: Variable cells

Expansion ratio Expansion ratio is calculated as follows.

[0099]

$$\text{Expansion ratio} = \text{Density of non-foam} / \text{Density of foam}$$

[0100] The density was determined using a densimeter (Densimeter-H: Toyo Seiki Seisakusho). The non-foam is

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an article obtained by melting a polyethylenic foaming composition followed by cooling without foaming.

### Impact resilience

- 5 **[0101]** In compliance with JIS K6301, a prescribed iron rod was allowed to fall freely and hit against the test floor at room temperature. From the height from which the rod fell down and the height to which the rod bounced up, impact resilience (%) was determined and evaluated as follows.

- ⊙: Impact resilience of 20% or more  
10 o: Impact resilience of 10% or more and less than 20%  
X: Impact resilience less than 10%

### Example 1

- 15 **[0102]** 100 parts by weight of ethylenic copolymer powder (Bondfast 70B-P: Sumitomo Chemical, MFR = 90 g/10 minutes) consisting of 83% by weight of ethylene unit, 12% by weight of glycidyl methacrylate unit and 5% by weight of vinyl acetate, 20 parts by weight of adipic acid (primary dissociation constant in water  $K_1 = 3.7 \times 10^{-5}$ ), and 10 parts by weight of a foaming agent of a thermal decomposition type, namely, azodicarbonic amide (Cellmic C-191: Sankyo Chemical Co., Ltd., Decomposition temperature 210°C) were placed in a high-shear mixer (Supermixer SMV-20: Kawada Seisakusho), and the mixture was blended for 3 minutes at 500 rpm at room temperature to obtain a polyethylenic foaming composition powder.

**[0103]** The powder was dusted onto a plane mirror mold at 250°C, and allowed to stand for 12 seconds. Then the excessive powder was drained off.

- 25 **[0104]** The mold was then placed in a Geer oven at 230°C as the atmospheric temperature, and heated for 120 seconds to effect the foaming. Then the mold was taken out of the Geer oven and cooled in water to release the foam from the mold. The results of the evaluation of the foam obtained are shown in Table 1.

### Examples 2 to 9

- 30 **[0105]** Instead of adipic acid employed in Example 1, 10 parts by weight of succinic acid ( $K_1 = 6.4 \times 10^{-5}$ : Example 2), 10 parts by weight of isophthalic acid ( $K_1 = 6.4 \times 10^{-5}$ : Example 3), 10 parts by weight of terephthalic acid ( $K_1 = 29 \times 10^{-5}$ : Example 4), 2 parts by weight of fumaric acid ( $K_1 = 96 \times 10^{-5}$ : Example 5), 2 parts by weight of phthalic acid ( $K_1 = 110 \times 10^{-5}$ : Example 6), 2 parts by weight of oxalic acid ( $K_1 = 5400 \times 10^{-5}$ : Example 7), 2 parts by weight of dimeric acid (liquid dicarboxylic acid, Versadime, 216: Henkel Hokusui: Example 8) and 5 parts by weight of 1,3,5-benzenetricarboxylic acid (Nacalai Tesque: Example 9) were respectively employed, and the procedure otherwise similar to that in Example 1 was employed to obtain the respective foams. The results of evaluation are shown in Table 1.

### Examples 10 and 11

- 40 **[0106]** Instead of Bondfast 70B-P, ethylenic copolymer powder (Sumitomo Chemical, MFR = 280 g/10 minutes: Example 10) consisting of 85% by weight of an ethylene unit and 15% by weight of a glycidyl methacrylate unit and an ethylenic copolymer powder (Bondfast 20B: Sumitomo Chemical, MFR = 20 g/10 minute: Example 11) were respectively employed, and the procedure otherwise similar to that in Example 1 was employed to obtain the respective foams. The results of evaluation are shown in Table 1.

### Example 12

- 50 **[0107]** Except for using Bondfast 20B instead of Bondfast 70B-P and using 5 parts by weight of terephthalic acid instead of adipic acid, the procedure similar to that in Example 1 was employed to obtain a foam. The results of evaluation are shown in Table 1.

### Example 13

- 55 **[0108]** A foam was obtained similarly as in Example 12 except for employing adipic acid in the amount of 1 part by weight. The results of evaluation are shown in Table 1.

## Example 14

[0109] A foam was obtained similarly as in Example 12 except for employing adipic acid in the amount of 0.5 parts by weight. The results of evaluation are shown in Table 1.

## Example 15

[0110] A foam was obtained similarly as in Example 1 except for using ethylenic copolymer powder (Bondfast 7B: Sumitomo Chemical, MFR = 10 g/10 minutes) consisting of 83% by weight of an ethylene unit, 12% by weight of a glycidylmethacrylate unit and 5% by weight of a vinyl acetate unit instead of Bondfast 70B-P and 5 parts by weight of terephthalic acid instead of adipic acid. The results of evaluation are shown in Table 1.

## Example 16

[0111] A foam was obtained similarly as in Example 1 except for using ethylenic copolymer powder (Sumitomo Chemical, MFR = 10 g/10 minutes) consisting of 79% by weight of an ethylene unit, 6% by weight of a glycidylmethacrylate unit and 15% by weight of a vinyl acetate unit instead of Bondfast 70B-P and 10 parts by weight of terephthalic acid instead of adipic acid. The results of evaluation are shown in Table 1.

## Example 17

[0112] A foam was obtained similarly as in Example 1 except for using 5 parts by weight of terephthalic acid instead of adipic acid and using Cellmic C-1 (azodicarbonic amide, Sankyo Chemical Co., Ltd., decomposition temp.: 205°C) instead of Cellmic C-191. The results of evaluation are shown in Table 1.

## Example 18

[0113] A polyethylenic foaming composition powder was obtained similarly as in Example 1 except for using Bondfast 20B instead of Bondfast 70B-P and using 5 parts by weight of isophthalic acid instead of adipic acid.

[0114] The powder was dusted onto a plane mirror mold at 270°C, and allowed to stand for 12 seconds. Then the excessive powder was drained off.

[0115] The mold was then placed in a Geer oven at 250°C as the atmospheric temperature, and heated for 120 seconds to effect the foaming. Then the mold was taken out of the Geer oven and cooled in water to release the foam from the mold. The results of the evaluation of the foam obtained are shown in Table 1.

## Comparative Example 1

[0116] A foam was obtained similarly as in Example 1 except for using no adipic acid. The results of evaluation are shown in Table 1.

## Comparative Example 2

[0117] A foam was obtained similarly as in Example 1 except for using polyethylene powder (Flo-thene UF-80: Sumitomo Seika, MFR = 75 g/10 minutes) instead of Bondfast 70B-P. The results of evaluation are shown in Table 1.

## Comparative Example 3

[0118] A foam was obtained similarly as in Example 1 except for using the thermoplastic elastomer powder obtained as described below instead of Bondfast 70B-P. The results of evaluation are shown in Table 1.

[0119] 50 parts by weight of an oil extended EPDM ( $ML_{1+4}$  100°C = 53) obtained by admixing 100 parts by weight of EPDM ( $ML_{1+4}$  100°C = 242, propylene content = 28% by weight, iodine value = 12) and 100 parts by weight of a mineral oil-based softener (Diana Process PW-380: Idemitsu Kosan), 50 parts by weight of propylene-ethylene random copolymer resin (ethylene content = 5% by weight, MFR = 90 g/10 minutes) and as a crosslinking coagent 0.4 parts by weight of a bismaleimide compound (Sumifine BM: Sumitomo Chemical) were mixed for 10 minutes in Banbury mixer, and then extruded as a pellet to obtain a master batch for partial crosslinking.

[0120] To 100 parts by weight of this master batch, 0.04 parts by weight of an organic peroxide, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane (Sanperox APO: Sanken Chemical Co., Ltd.) was added, and dynamic crosslinking was effected at 220°C using a twin screw kneader (TEX-44: Japan Steel Works, Ltd.) to obtain an elastomer composition

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pellet. After cooling this pellet with liquid nitrogen to  $-100^{\circ}\text{C}$ , the pellet was pulverized as frozen to obtain a thermoplastic elastomer powder for the powder molding which had the complex dynamic viscosity  $\eta^*$  (1) of  $6.4 \times 10^2 \text{ Pa.s}$  ( $6.4 \times 10^3 \text{ poise}$ ) and the Newtonian viscosity index  $n$  of 0.38. 99% by weight of this powder passed the 32 mesh screen of Tyler standard sieves.

## Comparative Example 4

[0121] A foam was obtained similarly as in Example 1 except for using 10 parts by weight of benzoic acid ( $K_1 = 6.3 \times 10^{-5}$ ) instead of adipic acid. The results of evaluation are shown in Table 1.

## Comparative Example 5

[0122] A foam was obtained similarly as in Example 1 except for using 5 parts by weight of polyacrylic acid (Aldrich, weight mean molecular weight: 2000) instead of adipic acid. The results of evaluation are shown in Table 1.

Table 1

	Appearance of foam	State of foam cells	Expansion ratio	Impact resilience
Example 1	⊙	⊙	4.5	⊙
Example 2	⊙	⊙	4.5	⊙
Example 3	⊙	⊙	4.8	⊙
Example 4	⊙	⊙	4.5	⊙
Example 5	o	⊙	4.2	⊙
Example 6	o	⊙	3.9	⊙
Example 7	⊙	⊙	1.7	o
Example 8	⊙	⊙	4.6	⊙
Example 9	⊙	⊙	5.7	⊙
Example 10	⊙	⊙	4.5	⊙
Example 11	⊙	⊙	3.8	⊙
Example 12	⊙	⊙	5.0	⊙
Example 13	⊙	⊙	4.3	⊙
Example 14	⊙	⊙	4.0	o
Example 15	⊙	⊙	4.6	⊙
Example 16	⊙	⊙	4.4	⊙
Example 17	⊙	⊙	5.5	⊙
Example 18	⊙	⊙	4.2	⊙
Comparative 1	⊙	⊙	3.5	X
Comparative 2	⊙	⊙	3.2	X
Comparative 3	⊙	⊙	3.5	X
Comparative 4	⊙	⊙	3.6	X
Comparative 5	⊙	⊙	3.7	X

## Example 19

[0123] 5000 g of the thermoplastic elastomer powder similar to that employed in Comparative Example 3 and 50 g of black pigment (PV-801, Sumika Color) were fed to a 20L Supremixer, and mixed at 500 rpm for 10 minutes to obtain a composition powder containing the thermoplastic elastomer for use in a non-foam layer.

[0124] Using two stainless cases (powder feeding boxes) shown in Figure 1 to 3, 4000 g of the composition powder for the non-foam layer was fed to one, and 4000 g of the polyethylenic foaming composition powder prepared similarly as in Example 1 was fed to the other. This case has rectangular opening 1 (600 mm x 220 mm), and has the depth of 210 mm, and was attached to single screw rotating device 3.

5 [0125] Separately, nickel embossed mold shown in Figure 4 to Figure 6, which had opening 4 similar in size to opening 1 provided on the powder feeding box shown in Figure 1, was pre-heated in a gas furnace. This mold had the thickness of 3 mm, and a complicated inner surface pattern, such as rope twist pattern 5 and leather grain pattern 6. Once the internal temperature of the mold became 300°C, the heated mold was placed with opening 4 facing down and meeting opening 1 on the powder feeding box containing the composition powder for non-foam layer described above, and the frames attached to the both openings were attached firmly to each other and fixed with clip 2, whereby achieving the integration. Once the surface temperature of the mold became 270°C, the powder feeding box containing the composition powder for non-foam layer was rotated by 180°, and the powder was allowed to be in contact with the mold for 7 seconds, whereby effecting the fusion. Immediately after this, the powder feeding box was rotated by 180° again to return to the lower position, and the excessive powder was allowed to fall down to the powder feeding box.

15 [0126] Immediately after this, opening 4 of the mold in which a non-foam layer had been molded was faced down and placed on opening 1 of the powder feeding box containing the polyethylenic foaming composition powder. The frames of the both openings were attached firmly to each other and fixed with clip 2, whereby achieving the integration. At this time, the surface temperature of the mold was 240°C. Immediately after this, the powder feeding box containing the polyethylenic foaming composition powder was rotated by 180 degrees, and the powder was allowed to be in contact with the mold for 15 seconds, whereby effecting the fusion. Immediately after this, the powder feeding box was rotated by 180 degrees again to return to the lower position, and the excessive powder was allowed to fall down to the powder feeding box.

25 [0127] The mold was released with opening 4 being facing down. The mold was further heated in a heating furnace at 230°C for 2 minutes to form a foam layer. After cooling, the foam was released to yield a molded composite foam consisting of a foam layer and a non-foam layer.

[0128] The molded composite foam thus obtained had the thickness of the non-foam layer of 0.5 mm and the thickness of the foam layer of 6.5 mm, and the rope twist pattern and the leather grain pattern had been transferred precisely on the surface of the non-foam layer. The foam layer showed no variation in the thickness and exhibited uniformity of the foamed cells. It had the expansion ratio of 4.5 and impact resilience of 20% or higher.

30 Example 20

[0129] A foaming composition powder was obtained similarly as in Example 1 except for employing Bondfast 20B instead of Bondfast 70B-P and 5 parts by weight of terephthalic acid instead of adipic acid.

35 [0130] The composition was heated under pressure at 130°C and 50 kg/cm<sup>2</sup> · G for 5 minutes using a press molding machine to obtain a sheet having the thickness of 1 mm.

[0131] The sheet was cut into 6 cm x 6 cm square pieces, which were inserted in the cavity of the mold which had previously been heated to 220°C, and then sandwiched between the iron plates whose surfaces had been coated with polyethylene terephthalate and which had been heated at the same temperature, and then heated under pressure at 10 kg/cm<sup>2</sup> · G for 60 seconds using a press which had been heated at the same temperature, and then taken out and allowed to stand to cool to obtain a foam. The result, of the evaluation are shown in Table 2.

40 Example 21

45 [0132] A foam was obtained similarly as in Example 20 except for employing 1 part by weight of adipic acid instead of terephthalic acid. The results are shown in Table 2.

Example 22

50 [0133] A polyethylenic foaming composition was obtained similarly as in Example 20 except for kneading was conducted using Laboplastmill (30C150: Toyo Seiki Seisakusho) at 120°C at 50 rpm for 5 minutes instead of using a high-shear mixer at a room temperature at 500 rpm for 3 minutes.

[0134] The composition was heated under pressure at 120°C and 50 kg/cm<sup>2</sup> · G using a press molding machine to obtain a sheet having the thickness of 1 mm.

55 [0135] The sheet was then foamed similarly as in Example 20 to obtain a foam. The results are shown in Table 2.

Comparative Example 6

[0136] A foam was obtained similarly as in Example 20 except that no terephthalic acid was used. The results of evaluation of the molded article obtained are shown in Table 2.

Comparative Example 7

[0137] A foam was obtained similarly as in Example 20 except for using 5 parts by weight of benzoic acid instead of terephthalic acid. The results of evaluation of the molded article obtained are shown in Table 2.

Comparative Example 8

[0138] The procedure similar as in Example 20 was employed except that 283.3 parts of the copolymer consisting of 91% by weight of an ethylene unit, 3% by weight of a maleic anhydride unit and 6% by weight of a methyl-acrylate unit (Bondine LX 4110: Sumitomo Chemical, MFR = 5 g/10 minutes, Maleic anhydride unit: Glycidyl methacrylate unit = 100:100 in this case) was employed instead of terephthalic acid and Cellmic C-191 was employed in the amount of 19.3 parts by weight. The results of evaluation of the molded article obtained are shown in Table 2.

Comparative Example 9

[0139] The procedure similar as in Example 20 was employed except that 13.4 parts of the copolymer consisting of 93% by weight of an ethylene unit and 7% by weight of an acrylic acid unit (A 201M: Mitsubishi Yuka, MFR = 7 g/10 minutes, Acrylic acid unit: Glycidyl methacrylate unit = 15:100 in this case) was employed instead of terephthalic acid and Cellmic C-191 was employed in the amount of 5.6 parts by weight. The results of evaluation of the molded article obtained are shown in Table 2.

Comparative Example 10

[0140] The procedure similar as in Example 20 was employed except that 88 parts of the copolymer consisting of 93% by weight of an ethylene unit and 7% by weight of an acrylic acid unit (A 201M: Mitsubishi Yuka, MFR = 7 g/10 minutes, Acrylic acid unit: Glycidyl methacrylate unit = 100:100 in this case) was employed instead of terephthalic acid and Cellmic C-191 was employed in the amount of 9.4 parts by weight. The results of evaluation of the molded article obtained are shown in Table 2.

Comparative Example 11

[0141] The procedure similar as in Example 20 was employed except that 61.7 parts of the copolymer consisting of 93% by weight of an ethylene unit and 7% by weight of an acrylic acid unit (A 201M: Mitsubishi Yuka, MFR = 7 g/10 minutes, Acrylic acid unit: Glycidyl methacrylate unit = 70:100 in this case) was used instead of terephthalic acid and Cellmic C-191 was employed in the amount of 8 parts by weight. The results of evaluation of the molded article obtained are shown in Table 2.

Example 23

[0142] According to the procedure in Example 20, a sheet having the thickness of 1 mm was obtained.

[0143] The sheet was cut into 6 cm x 6 cm square pieces, which were inserted in the cavity of the mold which had previously been heated to 220°C, and then sandwiched between the iron plates whose surfaces had been coated with polyethylene terephthalate and which had been heated at the same temperature, and then heated under pressure at 10 kg/cm<sup>2</sup> · G for 60 seconds using a press which had been heated at the same temperature, and then taken out and allowed to stand to cool to obtain a foam. The results of the evaluation of the molded article obtained are shown in Table 2.

Example 24

[0144] A foam was obtained similarly as in Example 23 except for using 2 parts by weight of adipic acid instead of terephthalic acid. The results of evaluation of the molded article obtained are shown in Table 2.

## Comparative Example 12

[0145] A foam was obtained similarly as in Example 23 except that no terephthalic acid was used. The results of evaluation of the molded article obtained are shown in Table 2.

## Comparative Example 13

[0146] A foam was obtained similarly as in Example 23 except for using 5 parts by weight of benzoic acid instead of terephthalic acid. The results of evaluation of the molded article obtained are shown in Table 2.

Table 2

	Appearance of foam	State of foam cells	Expansion ratio	Impact resilience
Example 20	⊙	⊙	5.8	⊙
Example 21	⊙	⊙	3.9	⊙
Example 22	⊙	⊙	5.4	⊙
Example 23	⊙	⊙	4.2	⊙
Example 24	⊙	⊙	5.8	⊙
Comparative 6	⊙	⊙	1.7	X
Comparative 7	⊙	⊙	1.6	X
Comparative 8	-	X	1.1	X
Comparative 9	X	o	1.5	X
Comparative 10	-	X	1.0	X
Comparative 11	-	X	1.2	X
Comparative 12	⊙	⊙	1.8	X
Comparative 13	⊙	⊙	1.8	X

[0147] In the Examples and Comparative Examples shown below, appearance of the top layer and the foam layer of a molded composite foam, thickness of the molded composite foam, state of foam cells of the foam layer, expansion ratio of the foam layer and impact resilience are evaluated as follows.

Appearance of top layer of molded composite foam

[0148] The top layer was observed macroscopically and evaluated as follows.

- o: No pinholes  
X: pinholes

Appearance of foam layer of molded composite foam

[0149] The foam layer was observed macroscopically and evaluated as follows.

- o: Uniform foaming without variation in thickness  
Δ: Almost uniform foaming with some variation in thickness  
X: Variable foaming with great variation in thickness  
XX: Almost no foaming

Thickness of molded composite foam

[0150] The thicknesses of the non-foam layer and the foam layer were determined using a dial gauge (Toyo Seiki Seisakusho).

State of foam cells of foam layer

[0151] Sectional surface of a foam was observed macroscopically and evaluated as follows.

- 5 o: Uniform cells  
 Δ: Slightly variable cells  
 X: Variable cells

Expansion ratio of foam layer

10

[0152] The foam layer was delaminated and the expansion ratio was calculated as follows.

$$\text{Expansion ratio} = \text{Density of non-foam} / \text{Density of foam}$$

- 15 [0153] The density of the foam layer was determined using a densimeter (Densimeter-H: Toyo Seiki Seisakusho). The non-foam is an article obtained by melting a polyethylenic foaming composition similar to that used for the foam layer followed by cooling without foaming.

Impact resilience of molded composite foam

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[0154] In compliance with JIS K6301, a prescribed iron rod was allowed to fall freely and hit against the test floor at room temperature. From the height from which the rod fell down and the height to which the rod bounced up, impact resilience (%) was determined and evaluated as follows.

- 25 ◎: Impact resilience of 20% or more  
 o: Impact resilience of 10% or more and less than 20%  
 X: Impact resilience less than 10%

Complex dynamic viscosity of thermoplastic elastomer

30

[0155] Using Dynamic Analyzer Model RDS-7700 (Rheometrics Co.), the dynamic viscosities at 250°C and at the frequencies of 1 and 10 radian/sec were determined while added strain of 5% by parallel plate mode, and the complex dynamic viscosities  $\eta^*$  (1) and  $\eta^*$  (100) were calculated, respectively.

- 35 Reference Example 1 (Preparation of a thermoplastic elastomer powder)

[0156] 50 parts by weight of an oil extended EPDM ( $ML_{1+4}$  100°C = 53) obtained by admixing 100 parts by weight of EPDM ( $ML_{1+4}$  100°C = 242, propylene content = 28% by weight, iodine value = 12) and 100 parts by weight of a mineral oil-based softener (Diana Process PW-380: Idemitsu Kosan), 50 parts by weight of propylene-ethylene random copolymer resin (ethylene content = 5% by weight, MFR = 90 g/10 minutes) and as a crosslinking coagent 0.4 parts by weight of a bismaleimide compound (Sumifine BM: Sumitomo Chemical) were mixed for 10 minutes in Banbury mixer, and then extruded as a pellet to obtain a master batch for partial crosslinking.

40 [0157] To 100 parts by weight of this master batch, 0.04 parts by weight of 2,5-dimethyl-2,5-bis(t-butylperoxy) hexane (Sanperox APO: Sanken Chemical Co., Ltd.) was added, and dynamic crosslinking was effected at 220°C using a twin-screw kneader (TEX-44: Japan Steel Works, Ltd.) to obtain an elastomer composition pellet. After cooling this pellet with liquid nitrogen to -100°C, the pellet was pulverized as frozen to obtain a thermoplastic elastomer powder for the powder molding which had the complex dynamic viscosity  $\eta^*$  (1) of  $6.4 \times 10^2$  Pa.s ( $6.4 \times 10^3$  poise) and the Newtonian viscosity index n of 0.38.

45 [0158] 99% by weight of this powder passed the 32 mesh screen of Tyler standard sieves.

50

Reference Example 2 (Preparation of foaming composition powder)

[0159] 100 parts by weight of Bondfast 70B-P, 20 parts by weight of adipic acid and 5 parts by weight of Cellmic C-191 were placed in a high-shear mixer and mixed at a room temperature at 500 rpm for 3 minutes to obtain a polyethylenic foaming composition powder.

55 [0160] 99% by weight of this powder passed through the 32 mesh screen of Tyler standard sieves.



## Example 25

[0161] An embossed nickel plate mold (15 cm x 15 cm) was heated in a Geer oven at 300°C. When the surface temperature of the mold became 260°C, the thermoplastic elastomer powder obtained in Reference Example 1 was dusted and allowed to stand for 7 seconds. 5 seconds after draining the excessive powder off, the foaming composition powder obtained in Reference Example 2 was dusted and allowed to stand for 15 seconds, and the excessive powder was drained off.

[0162] The mold was then placed in a Geer oven at 240°C as the atmospheric temperature, and heated for 120 seconds to effect the foaming.

[0163] Then the mold was taken out of the Geer oven and cooled in water to release the molded composite foam from the mold.

[0164] The results of the evaluation of the molded composite foam obtained are shown in Table 3.

## Examples 26 to 30

[0165] Instead of adipic acid, 10 parts by weight of succinic acid ( $K_1 = 6.4 \times 10^{-5}$ : Example 26), 5 parts by weight of isophthalic acid ( $K_1 = 24 \times 10^{-5}$ : Example 27), 5 parts by weight of terephthalic acid ( $K_1 = 29 \times 10^{-5}$ : Example 28), 2 parts by weight of dimeric acid (Henkel Hakusui, liquid dicarboxylic acid, Versadime, 216: Example 29) and 5 parts by weight of 1,3,5-benzenetricarboxylic acid (Nacalai Tesque: Example 30) were respectively employed, and the procedure otherwise similar to that in Example 25 was employed to obtain the respective molded composite foams. The results of evaluation are shown in Table 3.

## Example 31

[0166] An embossed nickel plate mold (15 cm x 15 cm) was heated in a Geer oven at 300°C. When the surface temperature of the mold became 260°C, the thermoplastic elastomer powder obtained in Reference Example 1 was dusted and allowed to stand for 5 seconds. 5 seconds after draining the excessive powder off, the foaming composition powder obtained similarly as in Reference Example 2 except of using 100 parts by weight of Bondfast 20B instead of Bondfast 70B-P, 5 parts by weight of terephthalic acid instead of adipic acid, and 5 parts by weight of Cellmic C-121 (azodicarbonic amide: Sankyo Chemical Co., Ltd., Decomposition temperature: 206° C) instead of Cellmic C-191 as a foaming agent was dusted and allowed to stand for 15 seconds, and the excessive powder was drained off.

[0167] The mold was then placed in a Geer oven at 230°C as the atmospheric temperature, and heated for 150 seconds to effect the foaming to obtain a molded composite foam. The results of the evaluation are shown in Table 3.

## Example 32

[0168] A molded composite foam was obtained similarly as in Example 31 except for using 5 parts by weight of Cellmic C-1 (azodicarbonic amide: Sankyo Chemical Co., Ltd., decomposition temperature: 205°C) instead of Cellmic C-121. The results are shown in Table 3.

## Example 33

[0169] An embossed nickel plate mold (15 cm x 15 cm) was heated in a Geer oven at 300°C. When the surface temperature of the mold became 245°C, the thermoplastic elastomer powder obtained in Reference Example 1 was dusted and allowed to stand for 7 seconds. 5 seconds after draining the excessive powder off, the foaming composition powder obtained similarly as in Reference Example 2 except for using 2 parts by weight of phthalic acid ( $K_1 = 110 \times 10^{-5}$ ) instead of adipic acid and 5 parts by weight of CAP-500 (azodicarbonic amide: Sankyo Chemical Co., Ltd., Decomposition temperature: 150° C) instead of Cellmic C-191 was dusted and allowed to stand for 15 seconds, and the excessive powder was drained off. The mold was then placed in a Geer oven at 230°C as the atmospheric temperature, and heated for 120 seconds to effect the foaming to obtain a molded composite foam. The results of the evaluation are shown in Table 3.

## Example 34

[0170] A molded composite foam was obtained similarly as in Example 25 except for using as a foaming composition powder the composition powder obtained similarly as in Reference Example 2 except for using Bondfast 20B instead of Bondfast 70B-P and 1 part by weight of terephthalic acid instead of adipic acid. The results are shown in Table 3.

## Example 35

[0171] A molded composite foam was obtained similarly as in Example 25 except for using as a foaming composition powder the composition powder obtained similarly as in Reference Example 2 except for using Bondfast 20B instead of Bondfast 70B-P and 0.5 parts by weight of terephthalic acid instead of adipic acid. The results are shown in Table 3.

## Example 36

[0172] A molded composite foam was obtained similarly as in Example 25 except for using as a foaming composition powder the composition powder obtained similarly as in Reference Example 2 except for using Bondfast 7B instead of Bondfast 70B-P, 2 parts by weight of terephthalic acid instead of adipic acid, 5 parts by weight of Cellmic C-121 instead of Cellmic C-191 and a Geer oven at 250°C instead of the Geer oven at 240°C. The results are shown in Table 3.

## Example 37

[0173] A molded composite foam was obtained similarly as in Example 25 except for using as a foaming composition powder the composition powder obtained similarly as in Reference Example 2 except for using the ethylenic copolymer powder (Sumitomo Chemical, MFR = 280 g/10 minutes) consisting of 85% by weight of an ethylene unit and 15% by weight of a glycidylmethacrylate unit instead of Bondfast 70B-P and 2 parts by weight of terephthalic acid instead of adipic acid. The results are shown in Table 3.

## Example 38

[0174] A molded composite foam was obtained similarly as in Example 25 except for using the foaming composition powder obtained from 100 parts by weight of Bondfast 70B-P, 5 parts by weight of terephthalic acid and 5 parts by weight of Cellmic C-191 by kneading using Laboplastmill at 120°C at 50 rpm for 5 minutes followed by pulverizing as frozen instead of the foaming composition powder obtained in Reference Example 2. The results are shown in Table 3.

## Example 39

[0175] An embossed nickel plate mold (15 cm x 15 cm) was heated in a Geer oven at 300°C. When the surface temperature of the mold became 265°C, the thermoplastic elastomer powder obtained in Reference Example 1 was dusted and allowed to stand for 5 seconds. 5 seconds after draining the excessive powder off, the non-foaming composition powder obtained similarly as in Reference Example 2 except for using 100 parts by weight of Bondfast 20B as an ethylenic copolymer powder, 5 parts by weight of terephthalic acid instead of adipic acid and no foaming agent of a thermal decomposition type was dusted and allowed to stand for 3 seconds. After the excessive powder was drained off, the mold was placed in a Geer oven at 240°C as the atmospheric temperature, and heated for 30 seconds.

[0176] Immediately after this, the foaming composition powder obtained similarly as in Reference Example 2 except for using Bondfast 20B instead of Bondfast 70B-P and 5 parts by weight of terephthalic acid instead of adipic acid was dusted and allowed to stand for 15 seconds, and then the excessive powder was drained off.

[0177] The mold was placed in a Geer oven at 240°C as the atmospheric temperature, and heated for 180 seconds to effect the foaming. After cooling, the molded article was detached. The results of evaluation of the molded composite foam thus obtained are shown in Table 3.

## Comparative Example 14

[0178] A molded composite foam was obtained similarly as in Example 25 except for using as a foaming composition powder the composition powder obtained similarly as in Reference Example 2 except for using no adipic acid. The results of evaluation are shown in Table 3.

## Comparative Example 15

[0179] A molded composite foam was obtained similarly as in Example 25 except for using as a foaming composition powder the composition powder obtained similarly as in Reference Example 2 except for using as an ethylenic copolymer powder the thermoplastic elastomer powder which is a partially crosslinked composition of EPDM employed in Reference Example 1 and propylene/1-butene random block copolymer resin (complex dynamic viscosity  $\eta^*$  (1) = 1

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$\times 10^3$  Pa.s ( $1 \times 10^4$  poise), Newtonian viscosity index  $n = 0.41$ ). The results of evaluation are shown in Table 3.

## Comparative Example 16

- 5 [0180] A molded composite foam was obtained similarly as in Example 25 except for using as a foaming composition powder the composition powder obtained similarly as in Reference Example 2 except for using benzoic acid ( $K_1 = 6.3 \times 10^{-5}$ ) instead of adipic acid. The results of evaluation are shown in Table 3.

## Comparative Example 17

- 10 [0181] A molded composite foam was obtained similarly as in Example 25 except for using as a foaming composition powder the composition powder obtained similarly as in Reference Example 2 except for using polyacrylic acid (Aldrich, weight mean molecular weight = 2000) instead of adipic acid. The results of evaluation are shown in Table 3.

15

Table 3

		Appear- ance of top layer	Thickness of top layer (mm)	Appear- ance of foam layer	Thickness of foam layer (mm)	State of foamed cells	Expansion ratio	Impact resil- ience
20	Example 25	o	0.8	o	5.0	o	4.9	⊙
	Example 26	o	0.8	o	4.8	o	4.8	⊙
	Example 27	o	0.9	o	4.6	o	4.5	⊙
25	Example 28	o	0.8	o	5.1	o	5.2	⊙
	Example 29	o	0.8	o	4.6	o	4.5	⊙
	Example 30	o	0.8	o	4.4	o	4.7	⊙
30	Example 31	o	0.7	o	4.4	o	6.0	⊙
	Example 32	o	0.8	o	4.8	o	6.0	⊙
	Example 33	o	0.7	o	3.2	o	3.4	⊙
35	Example 34	o	0.8	o	3.8	o	4.0	⊙
	Example 35	o	0.8	o	3.5	o	3.8	o
	Example 36	o	0.8	o	3.0	o	3.8	⊙
40	Example 37	o	0.8	o	4.0	o	3.5	⊙
	Example 38	o	0.8	o	5.0	o	5.0	⊙
	Example 39	o	0.7+0.3	o	4.0	o	5.0	⊙
45	Comparative 14	o	0.8	o	3.6	Δ	3.5	X
	Comparative 15	o	0.8	o	3.5	o	3.5	X
	Comparative 16	o	0.8	o	3.6	Δ	3.6	X
50	Comparative 17	o	0.8	o	3.7	Δ	3.7	X

## Example 40

- 55 [0182] An embossed nickel plate mold (30 cm x 30 cm) was heated in a Gear oven at 300°C. When the surface temperature of the mold became 265°C, the thermoplastic elastomer powder obtained in Reference Example 1 was dusted and allowed to stand for 5 seconds. 5 seconds after draining the excessive powder off, the foaming composition powder obtained similarly as in Reference Example 2 except for using Bondfast 20B instead of Bondfast 70B-P, 5 parts by

weight of terephthalic acid instead of adipic acid, and 5 parts by weight of Cellmic C-121 instead of Cellmic C-191 as a foaming agent was dusted and allowed to stand for 15 seconds, and the excessive powder was drained off.

[0183] The mold was then placed in a Gear oven at 240°C as the atmospheric temperature, and heated for 150 seconds to effect the foaming.

[0184] The mold was then taken out from the Gear oven, and, after cooling, the molded composite foam was released from the mold.

[0185] Subsequently, the molded composite foam thus obtained was placed with the foam layer facing up on a mold for polyurethane which had previously been kept at 40°C. A mixture which had previously been prepared and containing polyol (RI-29: Takeda) and isocyanate (IS-DIP: Takeda) in the ratio of 100: 164 was then casted into the mold to form a rigid urethane layer, whereby obtaining a multilayer molded article, which was then taken out from the mold.

[0186] The multilayer molded article thus obtained had the thickness of the non-foam layer of 0.8 mm, the thickness of the foam layer of 4.8 mm and the thickness of the rigid urethane layer of 4.5 mm, and exhibited satisfactory adhesion between the foam layer and the rigid urethane layer, which was reflected as delamination in 180 degrees delamination test (at 23°C, tensile speed of 200 mm/minute).

#### Example 41

[0187] 5000 g of the thermoplastic elastomer obtained in Reference Example 1 and 50 g of black pigment (PV-801: Sumika Color) were fed to a 20L Supermixer and mixed at 500 rpm for 10 minutes to obtain a composition powder containing the thermoplastic elastomer to be used for a non-foam layer.

[0188] As shown in Figure 7, composition powder 9 obtained as above was introduced into vessel 7, and mold 8 for the powder molding which had previously been heated at 260°C and had a emboss pattern was placed with its opening being met with the opening of the vessel, and the frames attached to the both openings were attached firmly to each other and fixed, whereby effecting the integration.

[0189] Immediately after this, the integrated vessel and the mold were rotated for 7 seconds by means of single screw rotating device, and composition powder 9 was fed to the cavity of mold 8 for the powder molding and deposited onto the molding surface having the emboss pattern. After terminating the rotation, excessive powder was drained off into vessel 7.

[0190] Then, the vessel containing the foaming composition powder obtained similarly as in Reference Example 1 was attached to be integrated with the mold, which was then rotated for 15 seconds by means of the single screw rotating device. After adhesion and fusion of the foaming composition, excessive foaming composition powder was drained off into the vessel.

Subsequently, the mold was removed from the vessel, and the mold was heated at 230°C for 2 minutes to foam a foam layer. This was then cooled and solidified to yield molded composite foam 10 consisting of non-foam layer 11 and foam layer 12.

[0191] Then as shown in Figure 9, mold 8 for the powder molding which still retained molded composite foam 10 (top layer material) was transferred to thermoplastic resin molding stage, where integration with mold base 13 was effected to yield female mold 14 for the thermoplastic resin molding.

[0192] Subsequently, as shown in Figure 9, when thermoplastic resin molding female mold 14 and male mold 15 still remained open, molten thermoplastic resin 17 which was polypropylene resin (Sumitomo Noblen AX 568: Sumitomo Chemical, MFR = 65 g/10 minutes) which had been heated at 190°C was fed via resin passage 16 to the cavity between molded composite foam 10 retained in female mold 14 and male mold 15. The mold was closed by a press at the molding surface pressure of 50 kg/cm<sup>2</sup>, whereby completing the molding of thermoplastic resin 18. Thus, multilayer molded article 19 in which to player 10 (molded composite foam) and thermoplastic resin 18 were integrated was obtained as shown in Figure 10.

[0193] The sectional view of the multilayer molded article obtained is shown in Figure 11. This article had the thickness of the non-foam layer of 0.7 mm, the thickness of the foam layer of 4 mm and the thickness of the thermoplastic resin layer of 2.3 mm, and exhibited impact resilience of 20% or more, and had the emboss pattern which had been transferred, exhibiting satisfactory appearance.

Brief description of the drawings:

[0194]

Figure 1 shows a planar view of a powder feeding box.

Figure 2 shows a frontal view of a powder feeding box.

Figure 3 shows a lateral view of a powder feeding box.

Figure 4 shows a planar view of a mold.

Figure 5 shows a frontal view of a mold.

Figure 6 shows a lateral view of a mold.

Figure 7 shows a sectional view of a mold for a powder molding together with a vessel containing a resin composition for the powder molding.

5 Figure 8 shows a sectional view of a mold for a powder molding which retains a molded composite foam (top layer).

Figure 9 shows a sectional view indicating that a thermoplastic resin is fed from a male mold for thermoplastic resin molding to a mold for a powder molding which retains a molded composite foam (top layer) and is integrated with a mold base.

Figure 10 is a sectional view indicating a male mold and a female mold for a thermoplastic resin molding are closed.

10 Figure 11 shows a sectional view of a multilayer molded article consisting of a molded composite foam (top layer) and a thermoplastic resin layer.

# Legends:

15 [0195]

- 1: Opening
- 2: Clip
- 3: Single screw rotating device
- 20 4: Opening
- 5: Rope twist pattern in mold
- 6: Leather grain pattern in mold
- 7: Vessel
- 8: Mold for powder molding
- 25 9: Resin composition for powder molding
- 10: Molded composite foam (top layer)
- 11: Non-foam layer
- 12: Foam layer
- 13: Mold base
- 30 14: Female mold for thermoplastic resin molding
- 15: Male mold for thermoplastic resin molding
- 16: Passage for feeding thermoplastic resin
- 17: Molten thermoplastic resin
- 18: Thermoplastic resin layer
- 35 19: Multilayer molded article

# Claims

- 1. A polyethylenic foaming composition comprising (a) 100 parts by weight of an ethylenic copolymer having glycidyl groups consisting of 20 to 99.9% by weight of an ethylene unit, 0.1 to 30% by weight of the unit of a glycidyl ester of an unsaturated carboxylic acid or an unsaturated glycidyl ether and 0 to 50% by weight of an ethylenically unsaturated ester unit other than glycidyl ester, (b) 0.1 to 30 parts by weight of a carboxylic acid having 2 or more carboxyl groups and a molecular weight of 1500 or less, and (c) 0.1 to 20 parts by weight of a foaming agent of a thermal decomposition type.
- 40 2. A method of preparing a polyethylenic foaming composition comprising compounding (a) 100 parts by weight of an ethylenic copolymer having glycidyl groups consisting of 20 to 99.9% by weight of an ethylene unit, 0.1 to 30% by weight of the unit of a glycidyl ester of an unsaturated carboxylic acid or an unsaturated glycidyl ether and 0 to 50% by weight of an ethylenically unsaturated ester unit other than glycidyl ester, (b) 0.1 to 30 parts by weight of a carboxylic acid having 2 or more carboxyl groups and a molecular weight of 1500 or less, and (c) 0.1 to 20 parts by weight of a foaming agent of a thermal decomposition type.
- 45 3. A polyethylenic foam obtained by molding a polyethylenic foaming composition according to Claim 1.
- 50 4. A method of preparing a polyethylenic foam comprising molding a polyethylenic foaming composition according to Claim 1.
- 5. A composite foam consisting of a foam layer obtained from the powder of a polyethylenic foaming composition (A)

according to Claim 1 and a non-foam layer obtained from a powder of a composition containing a thermoplastic elastomer (B) having a complex dynamic viscosity  $\eta^*$  (1) of  $1.5 \times 10^4$  Pa.s ( $1.5 \times 10^5$  poise) or less and a Newtonian viscosity index n of 0.67 or less which is a composition consisting of an ethylene/ $\alpha$ -olefinic copolymeric rubber and a polyolefinic resin or a partially-crosslinked composition consisting of an ethylene/ $\alpha$ -olefinic copolymeric rubber and a polyolefinic resin.

6. A method of preparing a composite foam comprising lining a foam layer obtained from the powder of a polyethylenic foaming composition (A) according to Claim 1 to a non-foam layer obtained from a powder of a composition containing a thermoplastic elastomer (B) according to Claim 5 by the powder molding method.

7. A multilayer molded article consisting of a composite foam layer and a thermoplastic resin layer wherein said composite foam layer comprises a foam layer obtained from the powder of a polyethylenic foaming composition (A) according to Claim 1 and a non-foam layer obtained from a powder of a composition containing a thermoplastic elastomer (B) according to Claim 5.

8. A method of preparing a multilayer molded article consisting of a composite foam layer and a thermoplastic resin layer, comprising lining a foam layer obtained from the powder of a polyethylenic foaming composition (A) according to Claim 1 to a non-foam layer obtained from a powder of a composition containing a thermoplastic elastomer (B) according to Claim 5 to form said composite foam layer by the powder molding method followed by retaining said composite foam layer in one of the male/female molds while supplying a molten thermoplastic resin between said composite foam and the other mold and pressing the molds to each other to integrate said composite foam layer and said thermoplastic resin.

9. A multilayer molded article consisting of a composite foam layer and a thermosetting resin layer wherein said composite foam layer comprises a foam layer obtained from the powder of a polyethylenic foaming composition (A) according to Claim 1 and a non-foam layer obtained from a powder of a composition containing a thermoplastic elastomer (B) according to Claim 5.

10. A method of preparing a multilayer molded article consisting of a composite foam layer and a thermosetting resin layer, comprising lining a foam layer obtained from the powder of a polyethylenic foaming composition (A) according to Claim 1 to a non-foam layer obtained from a powder of a composition containing a thermoplastic elastomer (B) according to Claim 5 to form said composite foam layer by the powder molding method followed by retaining said composite foam layer in one of the male/female molds while supplying a thermosetting resin between said composite foam and the other mold and pressing the molds to each other to integrate said composite foam layer and said thermosetting resin.

#### Patentansprüche

##### 1. Polyethylenschäummasse, umfassend

(a) 100 Gewichtsteile eines ethylenischen Copolymers mit Glycidylgruppen, das aus 20 bis 99,9 Gew.-% Ethyleneinheiten, 0,1 bis 30 Gew.-% Einheiten eines Glycidylesters einer ungesättigten Carbonsäure oder eines ungesättigten Glycidylethers und 0 bis 50 Gew.-% Einheiten eines anderen ethylenisch ungesättigten Esters als dem Glycidylester besteht,

(b) 0,1 bis 30 Gewichtsteile einer Carbonsäure mit 2 oder mehr Carboxylgruppen und einem Molekulargewicht von 1500 oder weniger, und

(c) 0,1 bis 20 Gewichtsteile eines Treibmittels vom thermischen Zersetzungstyp.

##### 2. Verfahren zur Herstellung einer Polyethylenschäummasse, umfassend Mischen von

(a) 100 Gewichtsteilen eines ethylenischen Copolymers mit Glycidylgruppen, das aus 20 bis 99,9 Gew.-% Ethyleneinheiten, 0,1 bis 30 Gew.-% Einheiten eines Glycidylesters einer ungesättigten Carbonsäure oder eines ungesättigten Glycidylethers und 0 bis 50 Gew.-% Einheiten eines anderen ethylenisch ungesättigten Esters als dem Glycidylester besteht,

(b) 0,1 bis 30 Gewichtsteilen einer Carbonsäure mit 2 oder mehr Carboxylgruppen und einem Molekulargewicht von 1500 oder weniger, und

(c) 0,1 bis 20 Gewichtsteilen eines Treibmittels vom thermischen Zersetzungstyp.

3. Polyethylenschaum, erhalten durch Formen einer Polyethylenschäummasse nach Anspruch 1.
4. Verfahren zur Herstellung eines Polyethylenschaums, umfassend Formen einer Polyethylenschäummasse nach Anspruch 1.
5. Verbundschaum, bestehend aus einer Schaumschicht, die aus dem Pulver einer Polyethylenschäummasse (A) nach Anspruch 1 erhalten wurde, und einer Nichtschaumschicht, die aus dem Pulver einer Zusammensetzung erhalten wurde, die ein thermoplastisches Elastomer mit einer komplexen dynamischen Viskosität  $\eta^*$  (1) von  $1,5 \cdot 10^4 \text{ Pa} \cdot \text{s}$  ( $1,5 \cdot 10^5 \text{ Poise}$ ) oder weniger und einem Newtonschen Viskositätsindex  $n$  von 0,67 oder weniger enthält, das eine Zusammensetzung, die aus einem Ethylen- $\alpha$ -Olefin-Copolymerkautschuk und einem Polyolefinharz besteht, oder eine teilweise vernetzte Zusammensetzung ist, die aus einem Ethylen- $\alpha$ -Olefin-Copolymerkautschuk und einem Polyolefinharz besteht.
6. Verfahren zur Herstellung eines Verbundschaums, umfassend Kaschieren einer Schaumschicht, die aus dem Pulver einer Polyethylenschäummasse (A) nach Anspruch 1 erhalten wurde, auf eine Nichtschaumschicht, die aus einem Pulver einer Zusammensetzung erhalten wurde, die ein thermoplastisches Elastomer (B) nach Anspruch 5 enthält, durch das Pulverformverfahren:
7. Mehrschichtiges Formteil, bestehend aus einer Verbundschaumschicht und einer Schicht eines thermoplastischen Harzes, wobei die Verbundschaumschicht eine Schaumschicht, die aus dem Pulver einer Polyethylenschäummasse (A) nach Anspruch 1 erhalten wurde, und eine Nichtschaumschicht, die aus dem Pulver einer Zusammensetzung erhalten wurde, die ein thermoplastisches Elastomer (B) nach Anspruch 5 enthält, umfasst.
8. Verfahren zur Herstellung eines mehrschichtigen Formteils, bestehend aus einer Verbundschaumschicht und einer Schicht eines thermoplastischen Harzes, umfassend Kaschieren einer Schaumschicht, die aus dem Pulver einer Polyethylenschäummasse (A) nach Anspruch 1 erhalten wurde, auf eine Nichtschaumschicht, die aus einem Pulver einer Zusammensetzung erhalten wurde, die ein thermoplastisches Elastomer (B) nach Anspruch 5 enthält, wodurch die Verbundschaumschicht durch das Pulverformverfahren erzeugt wird, gefolgt von Zurückhalten der Verbundschaumschicht in einem Teil eines Stempel-Gesenk-Formpaars, während ein geschmolzenes, thermoplastisches Harz zwischen den Verbundschaum und den anderen Teil des Formpaars zugeführt wird, und Zusammenpressen der Formen, wodurch die Verbundschaumschicht und das thermoplastische Harz zusammengefügt werden.
9. Mehrschichtiges Formteil, bestehend aus einer Verbundschaumschicht und einer Schicht eines hitzehärtbaren Harzes, wobei die Verbundschaumschicht eine Schaumschicht, die aus dem Pulver einer Polyethylenschäummasse (A) nach Anspruch 1 erhalten wurde, und eine Nichtschaumschicht, die aus dem Pulver einer Zusammensetzung erhalten wurde, die ein thermoplastisches Elastomer (B) nach Anspruch 5 enthält umfasst.
10. Verfahren zur Herstellung eines mehrschichtigen Formteils, bestehend aus einer Verbundschaumschicht und einer Schicht eines hitzehärtbaren Harzes, umfassend
 

Kaschieren einer Schaumschicht, die aus dem Pulver einer Polyethylenschäummasse (A) nach Anspruch 1 erhalten wurde, auf eine Nichtschaumschicht, die aus einem Pulver einer Zusammensetzung erhalten wurde, die ein thermoplastisches Elastomer (B) nach Anspruch 5 enthält, wodurch die Verbundschaumschicht durch das Pulverformverfahren erzeugt wird, gefolgt von Zurückhalten der Verbundschaumschicht in einem Teil eines Stempel-Gesenk-Formpaars, während ein hitzehärtbares Harz zwischen den Verbundschaum und den anderen Teil des Formpaars zugeführt wird, und Zusammenpressen der Formen, wodurch die Verbundschaumschicht und das hitzehärtbare Harz zusammengefügt werden.

#### Revendications.

1. Composition moussante polyéthylénique comprenant (a) 100 parties en masse d'un copolymère éthylénique ayant des groupes glycidyle consistant en 20 à 99,9% en masse d'une unité d'éthylène, 0,1 à 30% en masse de l'unité d'un glycidylester d'un acide carboxylique insaturé ou d'un glycidyléther insaturé et 0 à 50% en masse d'une unité d'ester éthyléniquement insaturé différente d'un glycidylester, (b) 0,1 à 30 parties en masse d'un acide carboxylique ayant 2 ou plusieurs groupes carboxyle et une masse moléculaire de 1500 ou moins, et (c) 0,1 à 20 parties en

masse d'un agent moussant d'un type à décomposition thermique.

2. Procédé de préparation d'une composition moussante polyéthylénique comprenant la combinaison (a) de 100 parties en masse d'un copolymère éthylénique ayant des groupes glycidyle consistant en 20 à 99,9% en masse d'une  
 5 unité d'éthylène, 0,1 à 30% en masse de l'unité d'un glycidylester d'un acide carboxylique insaturé ou d'un glycidyl-  
 éther insaturé et 0 à 50% en masse d'une unité d'ester éthyléniquement insaturé différente d'un glycidylester, (b)  
 0,1 à 30 parties en masse d'un acide carboxylique ayant 2 ou plusieurs groupes carboxyle et une masse moléculaire de 1500 ou moins, et (c) 0,1 à 20 parties en masse d'un agent moussant d'un type à décomposition thermique.
  
- 10 3. Mousse polyéthylénique obtenue par moulage d'une composition moussante polyéthylénique selon la revendication 1.
  
4. Procédé de préparation d'une mousse polyéthylénique comprenant le moulage d'une composition moussante polyéthylénique selon la revendication 1.
  
- 15 5. Mousse composite consistant en une couche de mousse obtenue à partir de la poudre d'une composition moussante polyéthylénique (A) selon la revendication 1 et en une couche autre qu'une mousse obtenue à partir d'une  
 poudre d'une composition contenant un élastomère thermoplastique (B) ayant une viscosité dynamique complexe  $\eta^*$  (1) de  $1,5 \times 10^4$  Pa.s ( $1,5 \times 10^5$  poises) ou moins et un indice de viscosité newtonien n de 0,67 ou moins qui est  
 20 une composition consistant en un caoutchouc copolymérique éthylène/ $\alpha$ -oléfinique et une résine polyoléfinique ou une composition partiellement réticulée consistant en un caoutchouc copolymérique éthylène/ $\alpha$ -oléfinique et une  
 résine polyoléfinique.
  
- 25 6. Procédé de préparation d'une mousse composite comprenant l'application en revêtement d'une couche de mousse obtenue à partir de la poudre d'une composition moussante polyéthylénique (A) selon la revendication 1 sur une  
 couche autre qu'une mousse obtenue à partir d'une poudre d'une composition contenant un élastomère thermoplastique (B) selon la revendication 5 par le procédé de moulage de poudres.
  
- 30 7. Produit moulé multicouche consistant en une couche de mousse composite et en une couche de résine thermoplastique où ladite couche de mousse composite comprend une couche de mousse obtenue à partir de la poudre  
 d'une composition moussante polyéthylénique (A) selon la revendication 1 et une couche autre qu'une mousse obtenue à partir d'une poudre d'une composition contenant un élastomère thermoplastique (B) selon la revendication 5.
  
- 35 8. Procédé de préparation d'un produit moulé multicouche consistant en une couche de mousse composite et en une couche de résine thermoplastique comprenant l'application en revêtement d'une couche de mousse obtenue à partir  
 de la poudre d'une composition moussante polyéthylénique (A) selon la revendication 1 sur une couche autre qu'une mousse obtenue à partir d'une poudre d'une composition contenant un élastomère thermoplastique (B)  
 40 selon la revendication 5 pour former ladite couche de mousse composite par le procédé de moulage de poudres suivie par le maintien de ladite couche de mousse composite dans l'un des moules mâle/femelle pendant l'apport  
 d'une résine thermoplastique fondue entre ladite mousse composite et l'autre moule et le pressage des moules l'un contre l'autre pour intégrer ladite couche de mousse composite et ladite résine thermoplastique.
  
- 45 9. Produit moulé multicouche consistant en une couche de mousse composite et en une couche de résine thermodurcissable où ladite couche de mousse composite comprend une couche de mousse obtenue à partir de la poudre  
 d'une composition moussante polyéthylénique (A) selon la revendication 1 et une couche autre qu'une mousse obtenue à partir d'une poudre d'une composition contenant un élastomère thermoplastique (B) selon la revendication 5.
  
- 50 10. Procédé de préparation d'un produit moulé multicouche consistant en une couche de mousse composite et en une couche de résine thermodurcissable comprenant l'application en revêtement d'une couche de mousse obtenue à  
 partir de la poudre d'une composition moussante polyéthylénique (A) selon la revendication 1 sur une couche autre qu'une mousse obtenue à partir d'une poudre d'une composition contenant un élastomère thermoplastique (B)  
 55 selon la revendication 5 pour former ladite couche de mousse composite par le procédé de moulage de poudres suivie par le maintien de ladite couche de mousse composite dans l'un des moules mâle/femelle pendant l'apport  
 d'une résine thermodurcissable entre ladite mousse composite et l'autre moule et le pressage des moules l'un contre l'autre pour intégrer ladite couche de mousse composite et ladite résine thermodurcissable.



Figure 1:

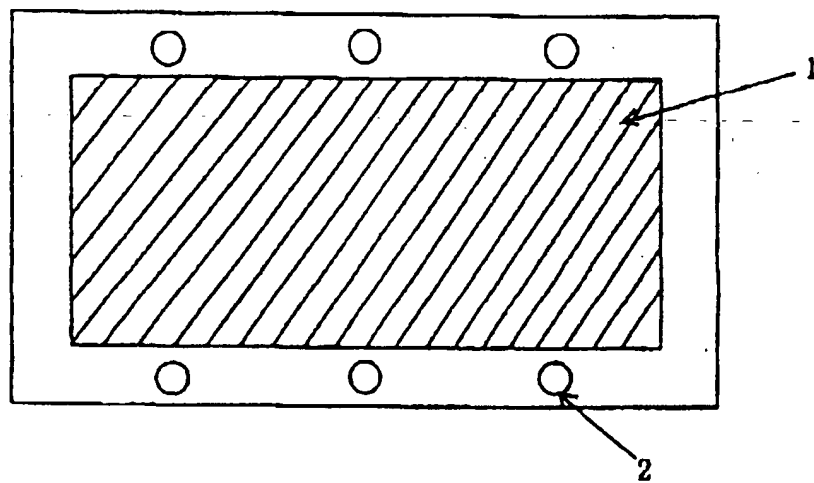


Figure 2:

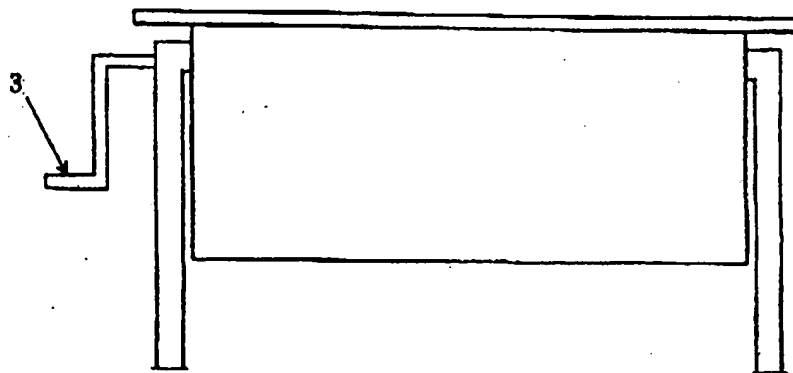


Figure 3:

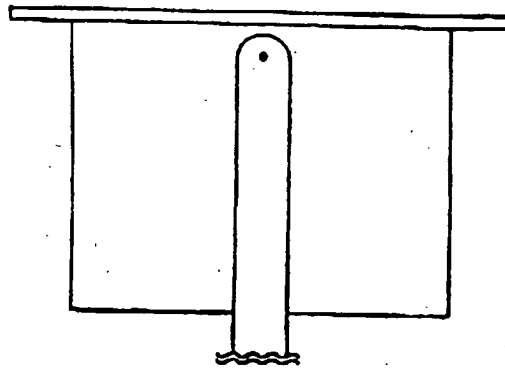


Figure 4:

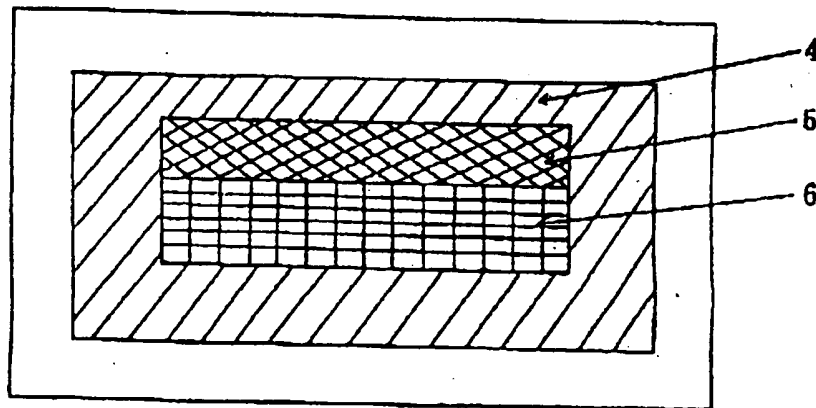


Figure 5:

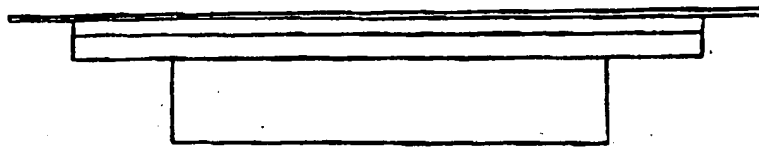


Figure 6:



Figure 7:

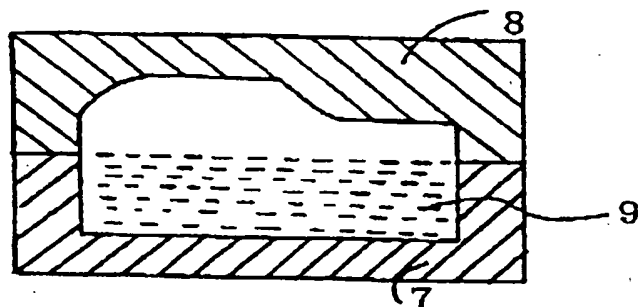


Figure 8:

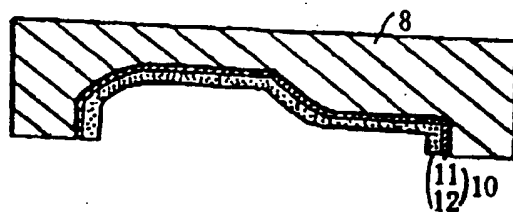


Figure 9:

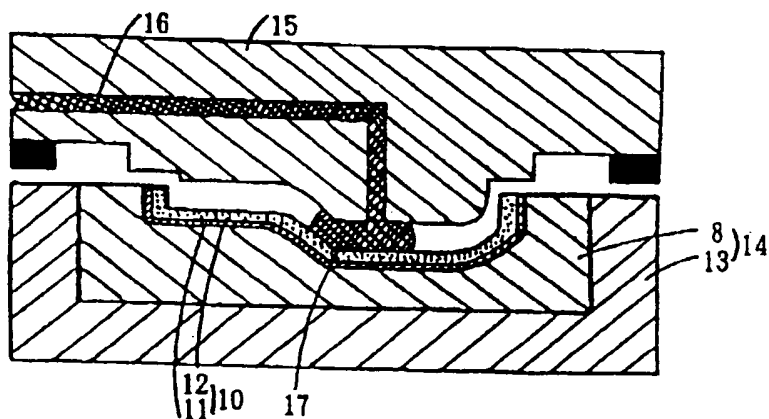


Figure 10:

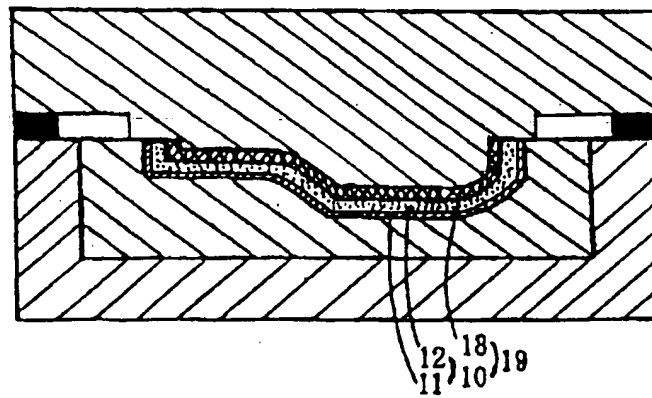
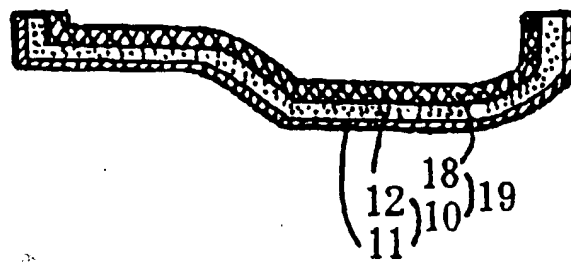


Figure 11:



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